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THE USE OF FOUR-PHOTON RAMAN SPECTROSCOPY FOR THE REMOTE SENSING OF NATURAL OBJECTS

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D. V. Mal'tsev

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16. Abstract

The results of the laboratory simulation of optical Kerr effect/Raman spectroscopy for the purpose of remote sensing are presented. The experimental setup is described, and measurements of the vibrational spectra of various liquids are obtained. Attention is given to the possibility of using the proposed method to detect trace hydrocarbons in water, and the spectrum of petroleum is obtained. Full-scale measurements using a laser spectrometer were made on the Black Sea.

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USE OF FOUR PHOTON RAMAN SPECTROSCOPY FOR THE LONG RANGE DIAGNOSTICS OF NATURAL OBJECTS

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D. V. Mal'tsev, and K. O. Surskii

1. In the last decade methods have been developed intensively */ 1256 for the long range diagnostics of the atmosphere and ocean. In this, along with the well tested passive optical methods which, basically, come down to measuring the spectra and the scattering indexes for the sunlight which passes through the atmosphere as well as that which is reflected and scattered by certain effective surface layers of the ocean [1, 2], active laser methods are also used [3, 4]. The optical methods for the diagnostics of the ocean have a great universality since they can be used from ships or from air and spacecraft and they can also give information about the surface of the water body, about some of the characteristics of the deep layers of the water and about the bottom. In this connection, steps directed towards the refinement of the optical methods for probing the ocean are a reality.

At the present time spontaneous Raman scattering (SKR), Rayleigh and Mie scattering (elastic scattering), and fluorometry are used as the traditional laser methods for the long range diagnostics of the ocean. On the other hand, we know that the methods of four-photon Raman spectroscopy, such as coherent antiStokes scattering of light (KARS) and the Kerr optical effect induced by Raman scattering (KR) (OKKR) [5, 4] greatly exceed SKR and other linear methods with respect to

*Numbers in margin indicate pagination of foreign text.

the level of the recorded signal and the spectral, time, and spatial resolution. Therefore some important oceanographic problems which cannot be solved at the present time by means of the traditional laser methods for ocean diagnostics may find their solution within the framework of nonlinear KR spectroscopy if the technology and methods are created for long range measurements in KARS and OKKR.

2. The first studies in which it was proposed that four-photon KR spectroscopy be used for the long range measurements [7, 8] were in 1978-1981. In these there are evaluations of the signal which goes "backwards" induced by the elastic scattering of the KARS signal which is being propagated "forward" during four-wave mixing in water [7] as well as that probing radiation which is elastically scattered in the atmosphere and which undergoes VKR amplification during tuning of the frequency difference of the pumping waves to the KR-active molecular oscillations for different atmospheric gases [9].

In [9, 10] it was suggested that the rotation of the wave front (OVF) due to induced Mandelshtam-Brillouin scattering be used to create the KARS signal which is propagated "backwards" in the direction of the pumping source. Demonstration experiments were carried out in which the KARS spectrum of the symmetrical valence vibrations for the CS_2 molecule were obtained in the long range circuit after one laser flash. The disadvantage of such an approach is the need to fulfill quite rigorous conditions for phase synchronism which, for certain KR lines, gives angles in the range of 140-160° between the directions for the propagation of the pumping waves

and the backward-moving KARS signal (for the excitation of KARS in water) [9, 10] which makes the diagnostics from long distances more difficult.

It was shown in [11] that the use of Kerr's optical effect, induced by KR, for long range probing spectroscopy, in which one of the pumping waves undergoes OVF additionally in the medium being studied, overcomes the indicated disadvantage and gives panoramic vibrational spectra from distances limited only by the need to exceed the VRMB threshold for one of the pumping waves. In this case the recorded signal frequency ω_3 which is formed as the result of the four-wave process $\omega_1=\omega_1\mp\omega_2-\omega_2$ (where the condition $\omega_1-\omega_2=\Omega_R$ - Ω_R is the frequency of the KR-active molecular resonance - is obeyed for ω_1, ω_2 - is the frequency of the KR-active molecular resonance) has a divergence of 10^{-3} rad and it is propagated precisely at an angle of 180° to the direction of the pumping wave..

In this work the results are given of experiments in which vibrational spectra are obtained for various liquids by means of the long range version of OKKR (which in the following will be called DKKR) and the first experiments of this kind under full scale conditions are discussed.

3. The measurements were made on the apparatus which is shown, in simplified form, in Fig. 1 [12, 13]. The pumping waves are provided by radiation from thesecond harmonic of a single-frequency, YAG:Nd^{3+} laser (1) and a single mode dye laser (LK) using rhodamine 6Zh or phenylamine No. 160 which provide for the tuning of λ_2 in the range 555-585 and 600-640 nm. The power of the pumping wave is $P \approx P_2 \approx 1$MW,

$\tau_{имп}=20$ ns, the width of the generation spectrum of the LK is $\Delta\nu_2 \approx 1\ см^{-1}$. The pumping waves E_1, E_2 were focused at an angle of 1° with respect to one another by means of a spherical mirror in the liquid being investigated, which has been poured into an open cuvette 9. The linear polarization of the wave E_1 is accentuated by a calcite prism 6, the wave E_2 was was linearly polarized (its polarization was accentuated by introducing a Glan prism) $\varphi=e_1 \hat{} e_2=60°$ (φ is the angle between the polarization cross cuts of the waves E_1, E_2). In this case, when the coherent background must be suppressed in the OKKR signal, which is due to the nonresonance part of the cubic permeability of the medium $\chi^{(3)NR}$ [5. 6], the Fresnel rhombus is additionally introduced into the wave E_2, which provides for the circular polarization of the pumping wave over a rather broad range of wavelengths. The photomultiplier 11 recorded the energy of the depolarized part of the wave $E_{ВБ}$ ($E_{рас}$), which was diverged by the calcute prism 6 and isolated from the noncoherent illuminations by a system of diaphragms and mirrors. At the same time, the energy of the waves $E_{изл}$ and E_2 in each laser pulse was measured by the photoreceivers 12. All of the signals were worked up in a computer which also corrected the scanning frequency of the LK and fed the spectra into the television display and the recorder. 1258

The laboratory measurements were made in ethanol and in aqueous solutions of benzene, ethanol, and petroleum. The waves E_1 and E_2 were focused within the liquids being studied through the open surface. The wave $E_{изл}$, which arises in the liquids due to VRMB and which is propagated towards E_1, becomes elliptically polarized in the presence of E_2, in which

case its polarization parameters, as in the case of ordinary OKKR, depend on the precision of tuning $(\omega_1-\omega_2)$ to Ω_R.

In the case of linear polarization of the pumping wave, for a wave intensity of $E_{1\,\text{накр}}(\omega_1)$ we get the following for the KR line of Lorentz form [5, 6]:

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$$I_{1\,\text{накр}} \sim \left| \frac{2}{3} + \sum_{j=1}^{N} \frac{(1-\rho_j)\,\tilde{\chi}^{Rj}_{1111}/\chi^{(3)\,NR}_{1111}}{-i-(\omega_1-\omega_2-\Omega_{Rj})/\Gamma_j} \right|^2 I_2^2 I_{1\,\text{пр}}. \qquad (1)$$

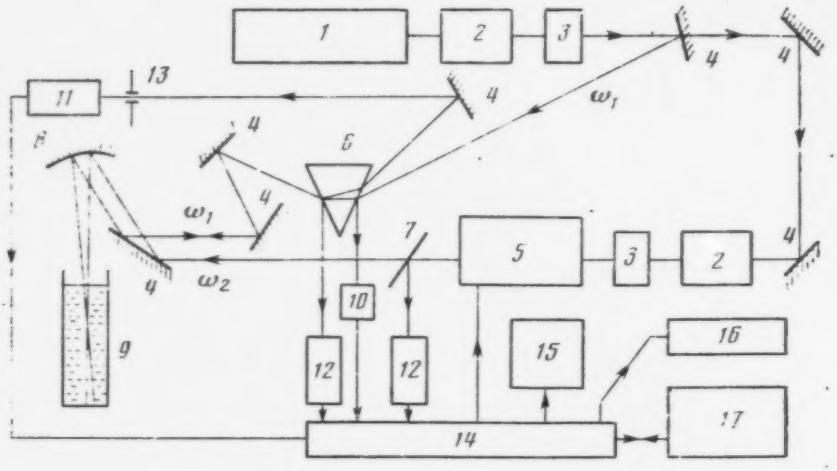

Fig. 1. Diagram of the apparatus for the laboratory modeling of the long range OKKR spectroscopy: 1) Master laser; 2) amplifiers; 3) frequency splitters; 4) mirrors; 5) dye laser; 6) calcite prism; 7) light splitter; 8) focusing mirror; 9) cuvette with the sample solution; 10-12) photoreceivers; 13) diaphragm; 14-17) microcomputer with peripheral attachments.

In the case of circular polarization of the wave E_2

$$I_{1\,\text{накр}} \sim \left| \sum_{j=1}^{N} \frac{(1-\delta\rho_j)\,\tilde{\chi}^{Rj}_{1111}/\chi^{(3)\,NR}_{1111}}{-i-(\omega_1-\omega_2-\Omega_{Rj})/\Gamma_j} \right|^2 I_2^2 I_{1\,\text{пр}}. \qquad (2)$$

In (1) and (2) δ_j is the degree of depolarization of the KR lines, $\tilde{\chi}^{Rj}_{1111}$ is the peak values of the resonance parts of the cubic permeability of the medium $\chi^{(3)}_{1111}$, $\chi^{(3)}$.

is the nonresonance part of the permeability, Γ_j is the half width of the KR lines. From (2) we can see that in the case of circular polarization for E_2 there is a suppression of the coherent background due to $\bar{\chi}^{(3)NR}_{1111}$. 1259

In all of the experiments a powerful signal $I_{\text{имп}}(\omega_1)$, was recorded which was attentated by more than 10^4 times to avoid damage to the photomultiplier. The signal disappeared completely upon blocking the wave E_2, i.e. it arose as the result of the four-photon process $\omega_1=\omega_2-(\omega_2-\omega_1)$.

4. The spectra of the DKKR lines for ethanol with a frequency of $\Omega_0/2\pi c=890$ см$^{-1}$ are shown in Fig. 2 for the case of linear (a) and circular (b) polarization of the wave E_2. We can see that in the long range geometry the OKKR spectrum is recorded distinctly, the relative measuring error does not exceed 20%.

An important question from the standpoint of practical application is to clarify the capabilities of DKKR in recording small impurities in water, particularly the observation and identification of background concentrations of hydrocarbons in connection with the need for a rapid diagnosis of petroleum contaminations in water supplies. From this standpoint the problem arises of determining the minimum concentration of benzene in water, recorded by means of DKKR, since aromatic hydrocarbons are present in the composition of many petroleum products.

The solubility of benzene in water is small (0.08%), therefore in the first stage of the experiments the measuring method was worked out on mixtures of benzene and ethanol, each of which has a single strong and rather narrow (($\Gamma<5$ см$^{-1}$)) KR line in the 900-1000 cm^{-1} range.

The panoramic DKKR spectra for solutions of benzene and ethanol in concentrations of 1400 and 350 million^{-1} in the 850-1000 cm^{-1} range are given in Fig. 3. The nondispersing pedestal of the spectra is related with the coherent background which is not totally suppressed and which is due to the contribution from electronic and Kerr nonlinearity to the DKKR signal. Maxima can be seen which correspond to the lines of ethanol with a frequency $\Omega_R/2\pi c$=890 cm^{-1} and benzene $\Omega_R/2\pi c$=992 cm^{-1}

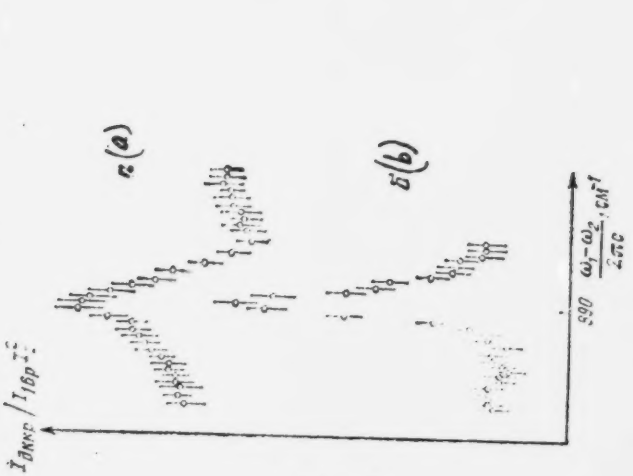

Fig. 2

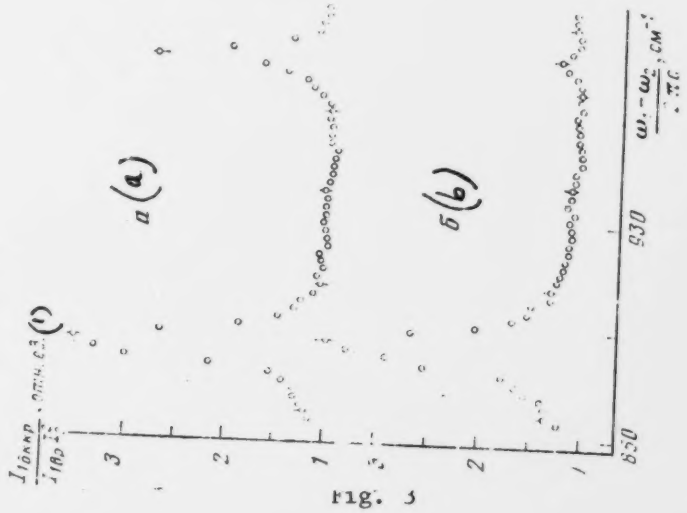

Fig. 3

Fig. 2. DKKR spectra of ethanol (the line $\Omega_R/2\pi c$=890 cm^{-1},): a) both pumping waves are linearly polarized $e_1 \wedge e_2 = 60°$; b) the wave $E_2(\omega_2)$ is circularly polarized.

Fig. 3. DKKR spectra for solutions of benzene and ethanol for relative concentrations of 1400 million^{-1} (a) and 350 million^{-1} (b).

KEY: 1. Relative units.

AFter removing the parasite depolarizations in the optical elements of the apparatus it became possible to record benzene in water. The spectrum for a solution of benzene in water with a concentraion of 30 million^{-1} is given in Fig. 4 (the vertical lines show the absolute errors in the measurement); the signal at each spectral point was

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accumulated for every 50 flashes. The minimum benzene concentration which was observable in our experiments is limited by the incomplete suppression of the coherent background and the relatively large width of the dye laser's spectrum. It is estimated that a 2-3-fold reduction in the width of the LK's generating line with a two-fold suppression 1260 of the coherent background and an increase in the time of accumulating the signal would increase the sensitivity of the observation by an order of magnitude.

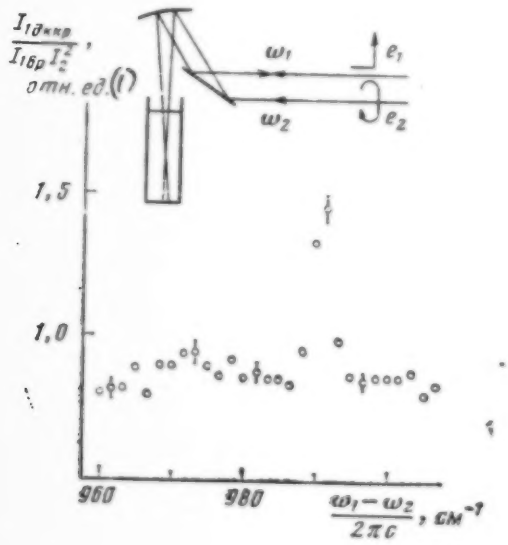

Fig. 4. The DKKR spectrum of benzene in water for a relative concentration of 30 million^{-1}. At the top the geometry of measurement.
KEY: 1. Relative units.

In a separate group of experiments solutions of various hydrocarbons in water were studied in the range of frequencies which correspond to the valence C-H vibrations (2800-3000 cm^{-1}). The measurements in this range of frequency tuning is complicated by the fact that the spectra for small impurities being studied is set against a backgroun of the wing of the OKKP spectrum for the O-H valnece vibrations which

must be subtracted correctly, first recording the spectrum for pure water in the computer. In addition, in our experiments, in those cases when their spectra become difficult to differentiate on the background of the signal's fluctuation because of the low hydrocarbon concentration, a special treatment of the OKKR signal was used [14] which allowed the signal/noise ratio to be increased significantly.

The OKKR spectrum of Caspian petroleum from "Banka Lam" is shown in Fig. 5 with the subtraction of the contribution from the wing of the KR bands for the valence vibrations of water and treatment by means of the algorithm suggested in [14]. The petroleum concentration in the water was varied in the range (1-0.1) x 10^{-4} (by volume). The samples were prepared using the ultrasonic dispersion of the raw petroleum in known volumes of water. We note that the concentrations are approximately one order of magnitude lower than the characteristic level of contamination of the water supply in ports, run off waters from petroleum refineries, etc. We can see from Fig. 5 that the sample of petroleum which was studied has a rich vibrational spectrum in the 3000-2900 cm^{-1} range where the strongest lines of the hydrocarbons are situated. A detailed calculation of the spectrum is a separate problem and can be carried out on a computer by means of comparing the frequencies of the maxima for the given spectrum with known frequencies of the strongest KR lines of the hydrocarbons which make up the given type of petroleum. However, at the present time the hydrocarbon composition of most petroleums is only known in its general features, therefore the interpretation of the OKKR spectrum shown in Fig. 5 requires special investigations.

5. Another possibility for long range probing of resevoirs by using OKKR spectroscopy uncovers the use of the radiation, which arises in the medium being studied due to the elastic scattering of one of the waves E_1, E_2 as one of the pumping waves. In this case there is no need to exceed the VRMB threshold for the wave E_1 and therefore it is possible to increase the distance between the OKKR spectrometer and the object being studied significantly.

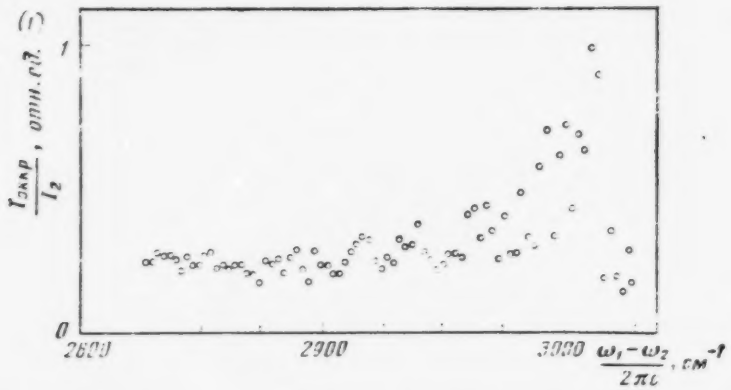

Fig. 5. The OKKR spectrum of petroleum from Banka Lam (Caspian Sea).

KEY: 1. Relative units.

The experiments modeling this type of long range diagnostics were carried out in ethanol in the range of frequency tuning 3000-2800 cm^{-1} in which three strong lines are found with frequencies $\Omega_R/2\pi c$=2974, 2928 and 2877 cm^{-1}, which correspond to the C-H valence vibrations. The measurements were made in the following way. Two linearly polarized 1261 waves E_1, E_2 ($e_1 e_2=\varphi=60^\circ$) were propagated so that they intersected at an angle of 2° in a cuvette containing the ethanol (l=80 см) in the direction of a photoreciever which recorded the OKKR spectrum. The length of the region of intersection of the waves E_1, E_2 was 8 cm. A diaphragm was placed in front of the photoreceiver which blocked the wave E_2 and the flashes associated with the scattering of the radiation

with a frequency ω_2 in the cuvette and on the optical elements.

The radiation with a frequency ω_2 was isolated in the beam E_1 by means of glass light filters and an MDR-4 monochromator. An analyzer (a Glan-Thomson prism) is placed in front of the monochromator and the filters and crossed with e_2 which isolates the depolarized part of the probing wave E_2 which is elastically scattered in the channel of the wave E_1. The photoreceiver (FEU-79), as in the case of ordinary OKKR, recorded the dependence of the energy of the depolarized part of E_2 during scanning $\omega_1-\omega_2$ near Ω_R (see (1)).

The OKKR spectra that were obtained are shown in Fig. 6 (a - recorded by the standard method and b - in the case in which an elastically scattered radiation was used for E_2). In the latter case the power of the recorded signal was 10^2-10^3 times lower than in the former and it was equal to (5-10) x 10^{10} photons per pulse (which corresponds to the standard level of the KARS signal in condensed media for excitation with pulsed lasers). The OKKR signal in these measurements can be observed visually through a monochromator. It arose on the background of the illumination associated with the residual depolarization of the elastic scattering. The KR lines with frequencies of 2974, 2928, and 2877 cm^{-1} (they are marked by arrows) which are situated on the pedestal due to the contribution from $\chi^{(3)NR}$ and are not completely suppressed by the flashes are clearly visible in Fig. 6.

6. An OKKR spectrometer was developed and produced to carry out full scale experiments. Its basic elements are the master laser and five amplifiers based on YAG:Nd^{3+} crystals (high quality crystals 8x100 mm in size were used in the final amplification cascades), thermostabilized frequency splitters based on a DSDA crystal, a dye laser with a tuning range for the generating wavelength of 580-640 nm, a focusing 23X telescope (d_{out} = 22 cm), a polarization analyzer and a photoreceiver. The spectrometer is assembled in the form of a single

unit. The operational control of the LK, the collection and treatment of the signals were accomplished with a microcomputer DVK-2M using a KAMAK panel.

The full scale experiments were carried out on the Black Sea in October, 1986. The spectrometer was set on the deck of a ship; the distance to the surface of the water was 2 m. The entire unit operated stably under conditions of the expedition however, because of the poor weather conditions, it was not possible to get the OKKR spectra of the organic impurities in the sea water in the long range method of measuring. Therefore these experiments will be continued in later expeditions.

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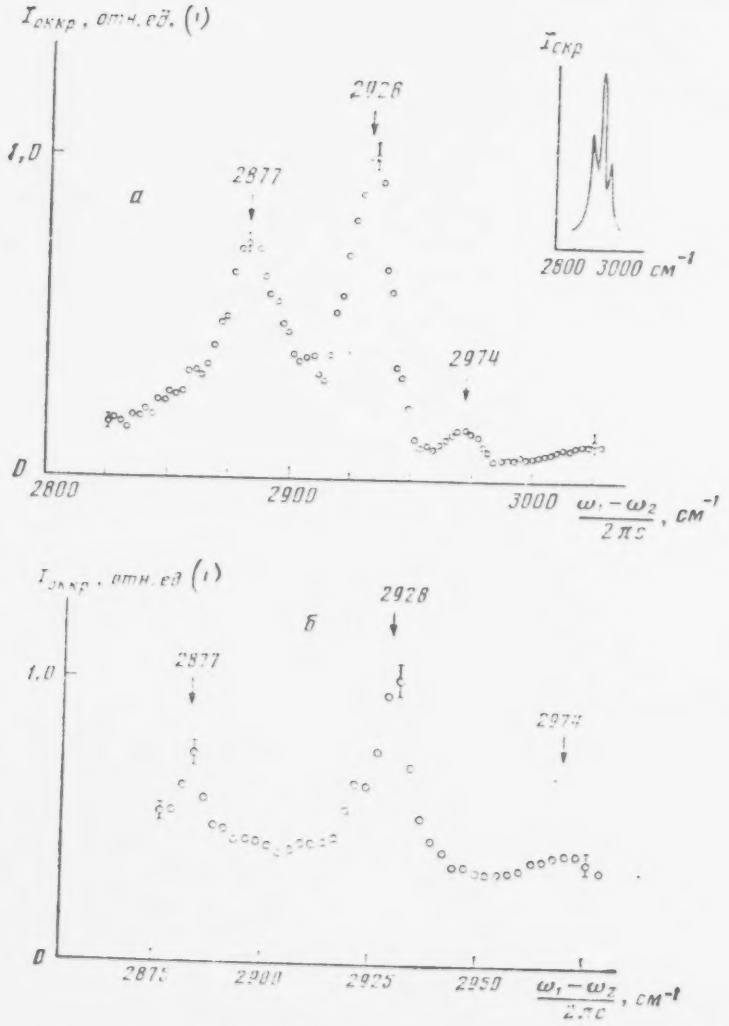

Fig. 6. The OKKR spectra of ethanol: a) in the 2800-3000 cm^{-1} range (the corresponding SKR spectrum at the top); b) spectrum obtained under conditions for which one of the interacting waves arose in the medium as the result of the elastic scattering of the pumping wave.

KEY: 1. relative units.

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